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One-Step Synthesis of Donor-Substituted Symmetric and Unsymmetric Trityl Cations from Arenes and Benzoic Acids

Yanick Schriefers, Yiwei Gong, Jas S. Ward, Kari Rissanen, and Florian F. Mulks*

Herein, it is reported that reacting electron-rich arenes and benzoic acids with trifluoromethanesulfonic anhydride gives convenient one-step and one-pot access to triphenylmethylium trifluoromethanesulfonates. This method enables the straightforward formation of these useful Lewis acids without external C1 sources. Three examples are isolated with one preparation upscaled to give 3 g of the trityl salt. Control experiments support a Friedel–Crafts acylation–alkylation sequence as the formation mechanism. Interestingly, the first Friedel–Crafts acylation is reversible, indicating a hydrolyzable C—C bond. These findings are envisioned to help design future synthetic processes to form trityl cation-based Lewis acids.

1. Introduction

Lewis acid catalysis is a foundational strategy in chemical synthesis.[1] The isolation of the first carbocation in 1891 marked a key moment in the development of this class of compounds.[2] Since then, carbocations have been extensively studied,[3] but are often unstable and not isolable.[3a] The triphenylmethyl (trityl) cation, as one of the oldest isolated stable carbocations,[1b,4] captured researchers' attention due to its robustness and unique reactivity, challenging the conventional view of carbocations as highly reactive intermediates.[5] Mesomeric stabilization in these ions paved the way for their broader applications. Trityl cation salts were extensively used in hydride abstraction reactions both in organic synthesis and in the investigation of mechanisms of organic and organometallic transformations.[6] They are also employed as catalysts in the Mukaiyama aldol,[7] Povarov,[8] Diels–Alder,[7b,9] and Friedel–Crafts reactions.[9b,10] We recently summarized the latest developments in the synthetic applications of trityl salts.[11]

Given the broad utility of trityl cations, the development of efficient and sustainable methods for their preparation is crucial. Traditional methods include the Friedel–Crafts alkylation of arenes with CCl_4 as C1 source mediated by $AlCl_3$, which can even be used to synthesize unsymmetric triphenylmethanols as trityl precursors (**Scheme 1**A).[12] Oestreich and co-workers prepared a helicene-like trityl cation from fluorenone in three steps.[13] A set of ferrocenyl tritylium complexes was synthesized through a two-step procedure involving the nucleophilic addition of 4-ferrocenylphenyllithium to the respective benzophenone and treating the resulting triarylmethanol with Brookhart's acid.[14] Laursen and co-workers synthesized a tris(2,4,6-trimethoxyphenyl)methylium salt, a cation revisited herein, through a four-step synthesis from 1,3,5-trimethoxybenzene and diethylcarbonate as C1 source.[15] Their route ends with an archetypical protonation of a triarylmethanol leading to water condensation (Scheme 1B). Pampaloni's group demonstrated an alternative: the decarbonylation of triphenylacetic acid chloride with high-valent metal halides leads to the formation of trityl cations.[16] Acid-catalyzed Friedel–Crafts reactions of benzaldehydes with benzene or other aromatic compounds demonstrate the use of oxidized toluene derivatives without external C1 source.[17] Significant strides have recently been made in the challenging synthesis of highly reactive electron-poor fluorinated trityl cations. Almost 60 years after Filler and Olah first detected the perfluorinated trityl cation $(C_6F_5)_3C^+$ in solution,[18] after seminal contributions by Dutton and Ozerov,[19] the group of Hasenstab-Riedel ultimately succeeded in isolating the salt $[(C_6F_5)_3C][Al(OTeF_5)_4]$ and $[(C_6F_5)_3C][Al(OTeF_5)_3Cl]$.[20] They synthesized the triarylmethanol precursor from a methylchloroformate C1 source with the aryl Grignard reagent and converted it to the triarylchloromethane (Scheme 1C). Reacting this with the corresponding Lewis and Brønsted acids to generate the trityl salts.[20] Ozerov's and Riedel's groups revisited this compound while we revised this work. Ozerov's group successfully isolated $[(C_6F_5)_3C][HCB_{11}Cl_{11}]$ and $[(C_6F_5)_3C][C_6F_5SCB_{11}Cl_{11}]$ at ambient temperature and Riedel's group isolated $[(C_6F_5)_3C][Ga_2Cl_7]$ in cryogenic conditions. Both syntheses involve relatively simple one-step procedures from stable precursors.[21]

Despite the increasingly widespread application of unsubstituted trityl salts, specialized substituted compounds are still rarely used. Recent breakthroughs toward even more electron-poor trityl cations are of fundamental interest; however, donor substitution of trityls can yield more stable and practical carbenium ions. Commonly, the synthesis of tritylium salts requires stringent conditions, metal catalysts, external C1 sources, and multiple steps, underscoring the need for a convenient synthetic approach for stable

Y. Schriefers, Y. Gong, F. F. Mulks
Institute for Organic Chemistry
RWTH Aachen University
Landoltweg 1, 52074 Aachen, Germany
E-mail: ff@mulks.ac

J. S. Ward, K. Rissanen
Department of Chemistry
University of Jyvaskyla
Survontie 9 B, P.O. Box 35, 40014 Jyväskylä, Finland

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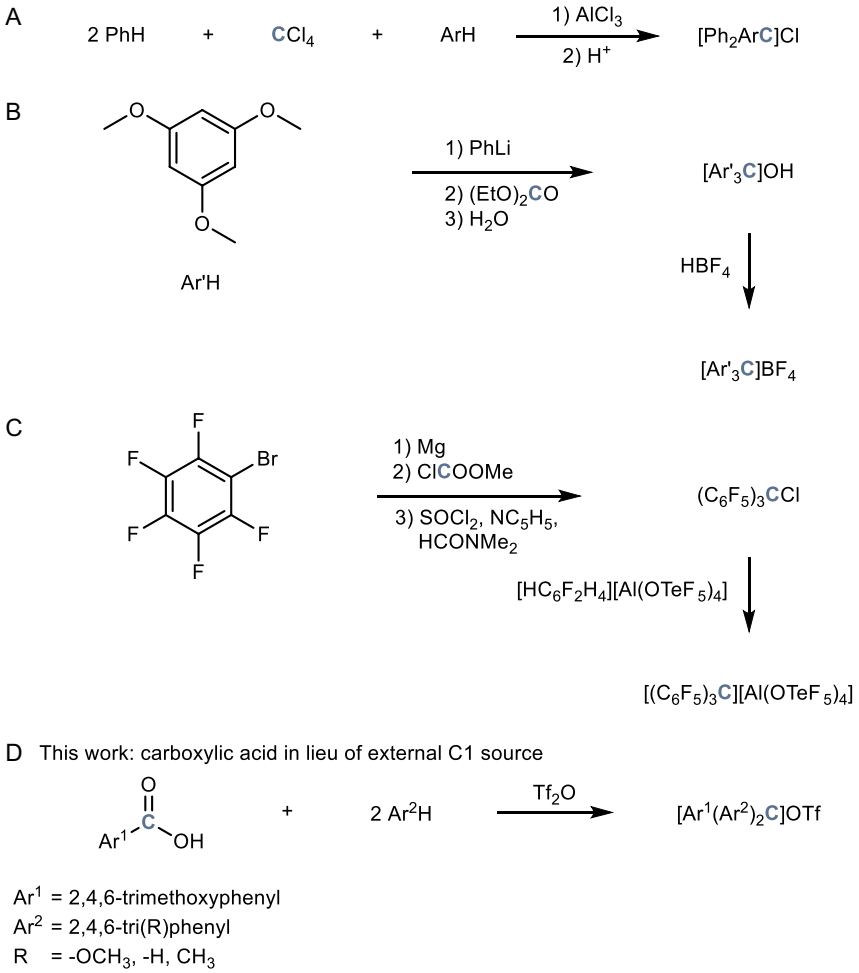
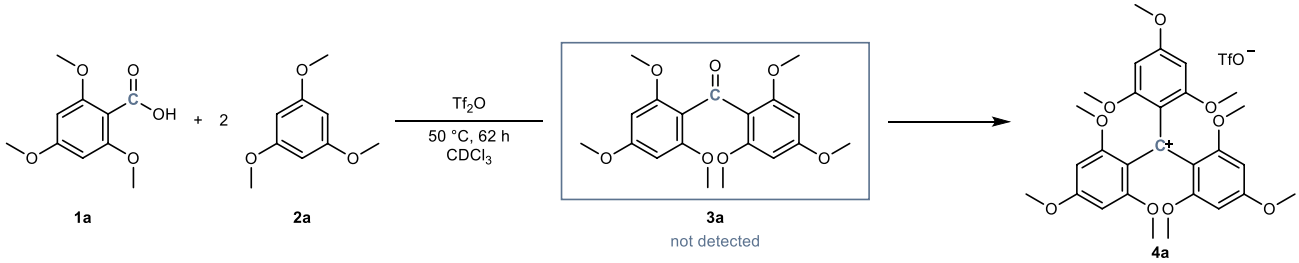


Scheme 1. Overview of related synthetic approaches to trityl cations and the synthetic approach of this work. A) A Friedel–Crafts strategy with tetrachloromethane as C1 source. B) A multistep process with diethylcarbonate as C1 source. C) Grignard additions to methylchloroformate as C1 source were used to make the precursors for perfluorinated trityl cations. D) Our one-step dehydrating Friedel–Crafts acylation–alkylation approach with a carboxylic acid instead of an external C1 source.

reagents. In this study, we present the discovery of a straightforward one-pot route to symmetric and unsymmetric donor-substituted tritylium trifluoromethanesulfonates (triflates, TfO^-) using carboxylic acids, arenes, and trifluoromethanesulfonic anhydride (Tf_2O).

2. Results and Discussion

We initially attempted to enhance the synthesis of the hexamethoxy-substituted benzophenone bis(2,4,6–trimethoxyphenyl) methanone **3a**. We employed the potent dehydration reagent Tf_2O in place of the commonly used trifluoroacetic anhydride (TFAA)[22] to initiate a Friedel–Crafts acylation with 2,4,6-trimethoxybenzoic acid **1a** and 1,3,5-trimethoxbenzene **2a** in $CDCl_3$ (**Scheme 2**). We hypothesized that the increased reactivity of Tf_2O would facilitate the synthesis of a wider range of benzophenone derivatives. To our surprise, the trityl cation tris(2,4,6-trimethoxyphenyl)methylium **4a** was detected in nuclear magnetic resonance (NMR) spectra rather than the ketone.



Scheme 2. Reaction scheme of our attempt to synthesize the ketone **3a** leading to the trityl triflate 4a.

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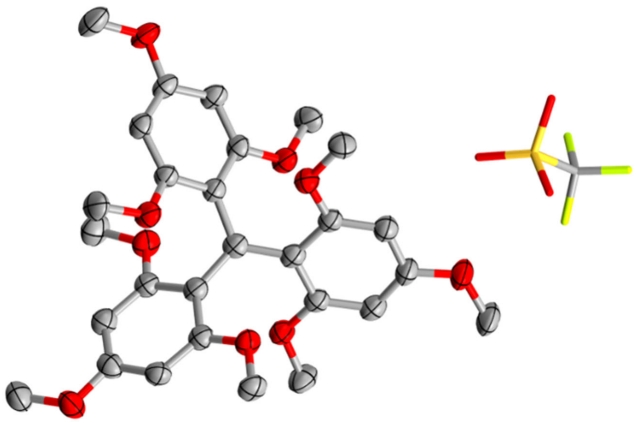
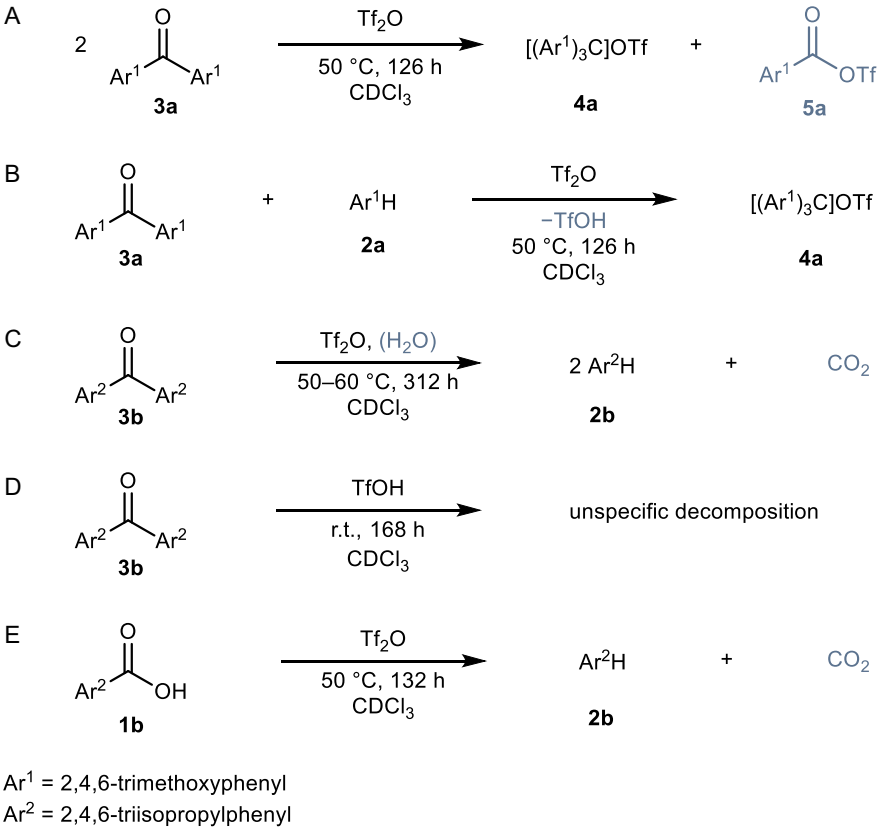


Figure 1. Molecular structure of **4a** in the solid state (hydrogen atoms omitted for clarity, carbon: gray, fluorine: bright green, sulfur: yellow). Thermal ellipsoids are shown at a probability level of 50%. Average bond length between $C_{central}$ and C_{aryl} 1.45 Å. Average out-of-plane rotation of aryls 38.5°.

Single crystals suitable for X-Ray diffraction were obtained from recrystallization of the precipitate in toluene (see **Figure 1**). Compound **4a** was isolated in the solid state in the monoclinic $P2_1/n$ space group as an unknown solvate, which was believed to be the crystallization solvent toluene, though ultimately had to be accounted for using Platon squeeze.[23] Even though numerous tritylium-based solid-state structures with different of anions have been reported,[24] only four incorporate the triflate anion.[25]

Our investigation provides a structure of the tris(2,4,6-trimethoxyphenyl)methylium cation with a triflate anion. The three $C_{central}$—C_{Ar} bond lengths in the planar triarylmethylium moiety of **4a** were found to be within the range of 1.429(4)—1.458(4) Å. These distances are within the 3σ tolerance interval of the corresponding bonds in the undecorated Ph_3COTf (1.44(1)—1.458(8) Å).[25c]

The surprising formation of **4a** prompted a mechanistic investigation (**Scheme 3**). First, a reaction of **3a** and triflic anhydride was attempted which, indeed, yielded the tritylium salt **4a**. The expected byproduct, carboxylic acid triflates **5a,** was not observed (Scheme 3A). This suggests that a retro-Friedel–Crafts acylation reaction can liberate the arene **2a** to undergo a Friedel–Crafts alkylation with an activated ketone **3a**. This hypothesis is supported by the observation of a seemingly increased yield when the reaction was performed in the presence of one equivalent of 2,4,6-trimethoxybenzene **2a** (Scheme 3B). Due to limited solubility of the trityl salts **4** in the reaction solvent, the accurate quantification of the products was not possible in solution. We found that bis(2,4,6-triisopropylphenyl)methanone **3b** was too hindered to form a trityl salt. Instead, it gave the arene **2b** when heated to 50 °C with Tf_2O (Scheme 3C). This was additionally confirmed by gas chromatography–mass spectrometry (GCMS) which showed only remaining carboxylic acid and the arene. This indicates cleavage through a retro-Friedel–Crafts acylation which requires a proton source such as residual moisture. An accelerated decomposition at room temperature with trifluoromethanesulfonic acid (TfOH) instead of Tf_2O supports this hypothesis (Scheme 3D).



Scheme 3. Control experiments at a 30 μmol scale. Gray colored compounds were not detected. A) Reaction of **3a** to **4a** with Tf_2O. B) Reaction of **3a** and **2a** to **4a** with Tf_2O. C) Decomposition of **3b** to **2b** with Tf_2O. D) Decomposition of **3b** with TfOH. E) Decomposition of **1b** to **2b** with Tf_2O.

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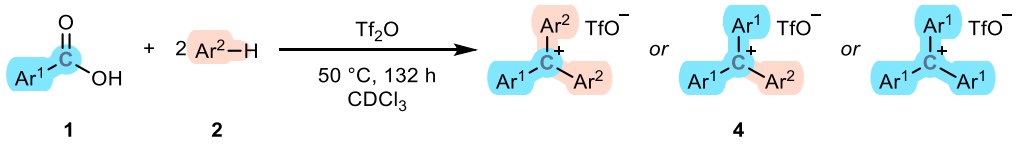
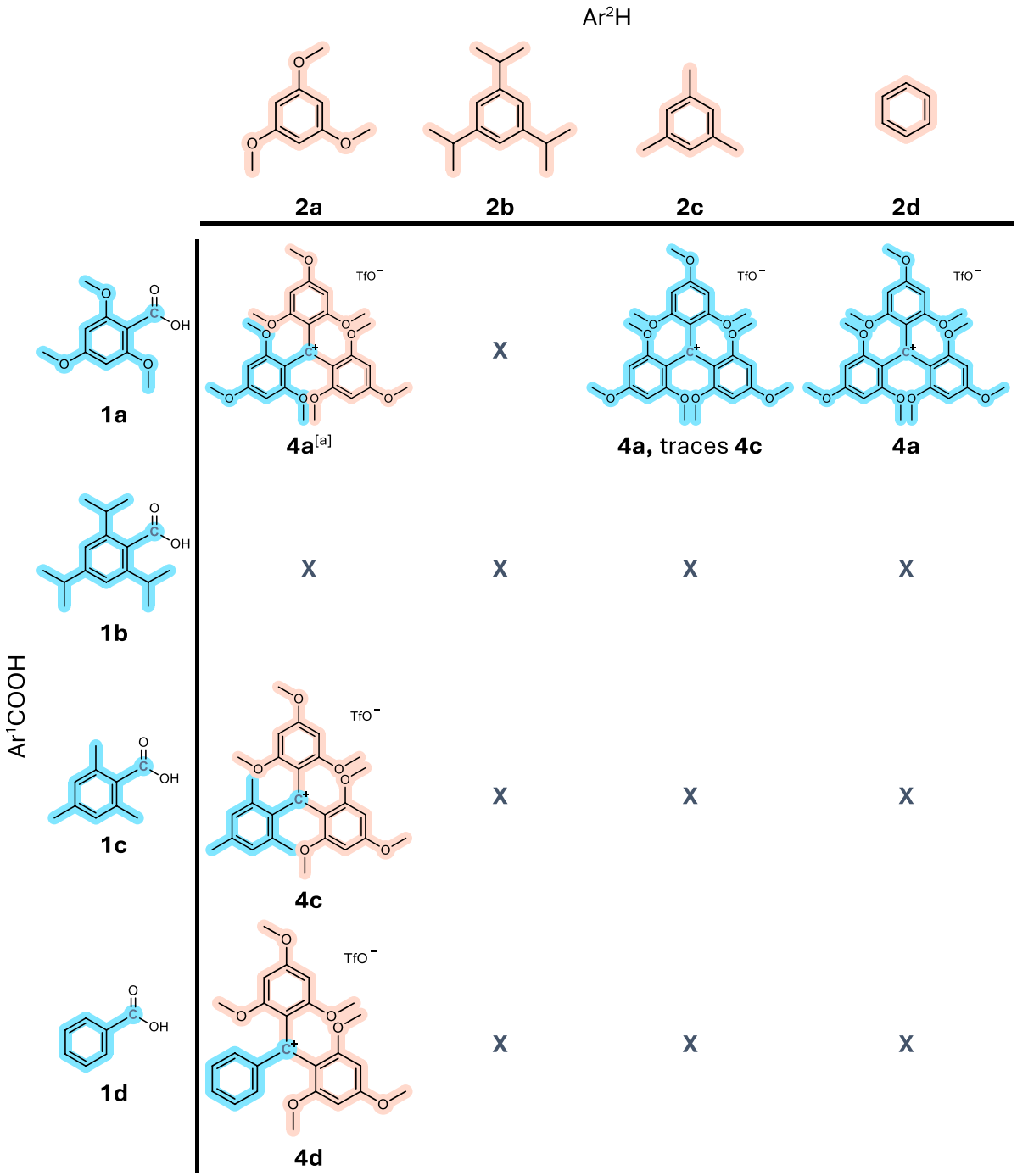


Scheme 4. Reaction scope investigation.

Table 1. Observed products of the reactions of substituted benzoic acids and substituted arenes with triflic anhydride.



[a]Reactions were performed in NMR tubes sealed with rubber septa at a 30 μmol scale in 650 μL $CDCl_3$. X = no **4** detected. A mixed origin of the arenes from **1a** and **2a** is possible due to retro-Friedel–Crafts reactions.

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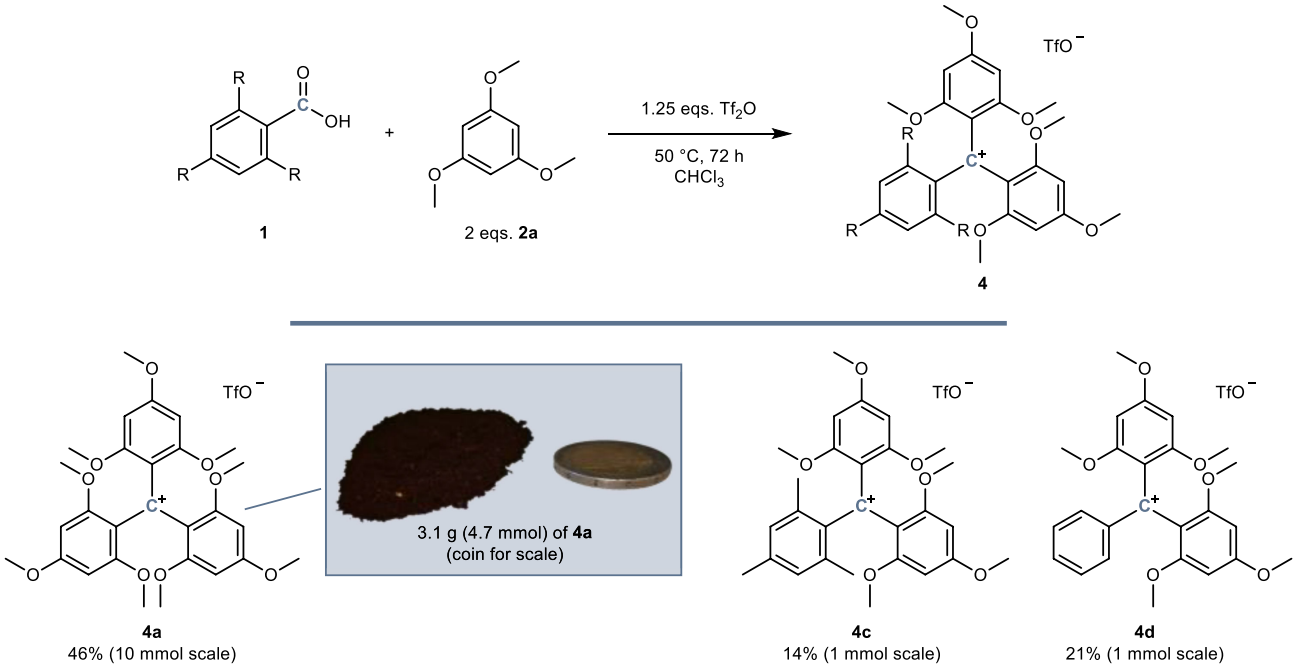
However, this reaction was unspecific, and we could not observe the arene. We also confirmed that the carboxylic acid **1b** reacts with Tf_2O at 50 °C to yield the arene **2b** (Scheme 3E). We even observed that the carboxylic acid **1a** slowly decarboxylated to give **2a** in untreated $CDCl_3$ in air. In contrast, it was stable when the solvent was stored over 4 Å molecular sieves which supports the involvement of moisture in this decomposition. This suggests that decarboxylation of the carboxylic acid triflates **5** occurs and explains why they were not observed as byproduct of retro-Friedel–Crafts acylation reactions.

We investigated the scope of this reaction with 1,3,5-OMe (**a**), -*i*Pr (**b**), -Me (**c**), and -H (**d**) substituents in a NMR scale study (**Scheme 4**, **Table 1**). Product identities were confirmed by ^{1}H, ^{13}C, and ^{19}F NMR and high-resolution MS (HRMS). As previously observed, the reaction with both methoxylated starting materials, benzoic acid **1a** and arene **2a**, yielded the trityl cation **4a**. 2,4,6-Triisopropylbenzoic acid **1b** failed to react with **2a**. Decomposition of **1b** to the arene **2b** was observed. The less sterically hindered 2,4,6-trimethylbenzoic acid **1c** and unsubstituted benzoic acid **1d** both reacted with **2a** to give the corresponding trityl cations **4c** and **4d**. The reaction of **1a** with the bulky 1,3,5-triisopropylbenzene **2b** showed no conversion. Interestingly, converting **1a** with **2c** or **2d** did not yield the anticipated trityl cations. In both cases, **4a** was detected instead. This phenomenon likely originates from the previously discussed retro-Friedel–Crafts acylation reactions, which supply the arene **2a**. The arene then reacts with an acylium ion sourced from the reaction of Tf_2O with **1a**, leading to the formation of **4a** as the main product in both experiments. This is further confirmed by the detection of trace amounts of **4c** in the reaction of **1a** with **2c**, which combines one substituent sourced from a retro-Friedel–Crafts reaction with one supplied as starting material. Syntheses lacking any electron-rich trimethoxylated starting material, in conjunction with all reactions involving bulky triisopropyl substituents, proved unsuccessful. The benzoic acids reacted in all cases, likely forming acylium salts and potentially undergoing further reactions.

The fact that only the methoxylated arene **2a** formed trityl cations can be explained with the mesomeric effect of the methoxy groups making this material more reactive toward nucleophilic addition (A_N) reactions which initiate the Friedel Crafts acylation. When attempting to prepare trityl cations with **1a** and the arenes **2b–d**, we either observed no trityl formation or the formation of the nonamethoxylated trityl cation salt **4a**. This can be rationalized through first decomposing **1a** in a retro-Friedel–Crafts reaction to give the activated arene **2a**. This arene is reactive enough to react with present acylium ions to form the tritylium ion (**Scheme 5**).

We subsequently aimed to isolate the promising target compounds **4a**, **4c**, and **4d** in larger scales (**Scheme 6**). The intense colors of the reaction solutions complicated the isolation via crystallization procedures. Purification ultimately succeeded by removal of the solvent in vacuo before subjecting the crude mixtures to column chromatography over silica gel using *n*-pentane/ethyl acetate and then ethyl acetate/methanol gradients as eluents. We selected **4a** for a 10 mmol scale reaction and isolated 3.12 g (4.71 mmol), equivalent to a yield of 46%. **4c** gave a poorer yield of 14% at a 1 mmol scale. The electronic activation of the methyl substituents does not appear to compensate the introduced steric hindrance. In contrast, we retrieved a promising weighing of 80% of **4d** from the more electron-poor but less bulky benzoic acid **1d**. However, an acetic acid impurity, likely formed through hydrolysis of EtOAc during or after chromatography, prompted further drying and filtration procedures resulting in a 21% final yield.



Scheme 5. Isolation of trityl salts.

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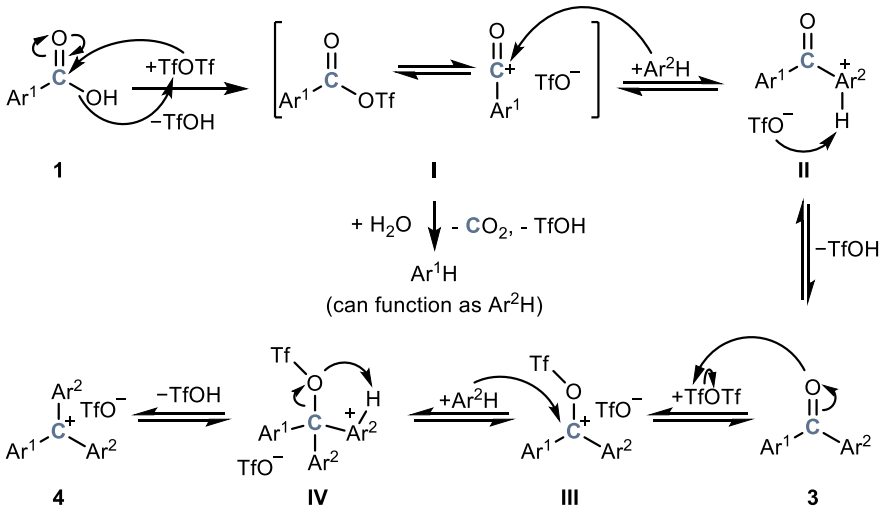
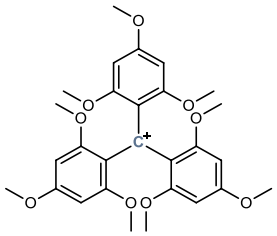
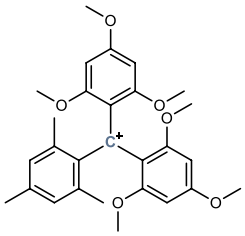
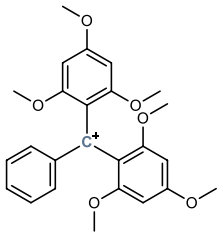
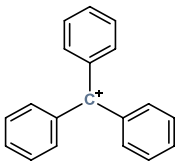


Scheme 6. Proposed reaction mechanism.

We propose that the formation of a trityl cation **4** starts with a transesterification of the carboxylic acid **1** with Tf_2O (Scheme 6). The resulting acid triflate can liberate an acylium ion **I**, which adds to arene **2** to form the Wheland intermediate **II**. Deprotonation gives the ketone **3**, which reacts with another equivalent of Tf_2O to form intermediate **III**. This intermediate can further react with another equivalent of **2**, affording **IV**. The final deprotonation restores aromaticity and leads to the product **4**.

We computed fluoride-ion affinities (*FIA*) and hydride-ion affinities (*HIA*) at the r²SCAN-3c/RIJCOSX[26] level of theory to judge the acidity of the products. The method choice was supported by a benchmark study by Greb and co-workers showing high performance in related chemistry.[27] Ion affinities were computed with Greb's modification of Krossing's anchor scheme using the Me_3SiF/Me_3Si^+ pair in lieu of free F^- (see Supporting Information).[28] Only the solvation energy of F^- and H^- was utilized for computing solution phase affinities. The FIA_{gas} values of the synthesized cations are 150–200 kJ mol^{-1} lower than the ones of the undecorated trityl cation Ph_3C^+, with the total values ranging from 451 (**4a**) to 504 (**4c**) kJ mol^{-1}. Solvation in dichloromethane (DCM) was modeled with a conductor-like polarizable continuum.[29] Acidity dampening stabilizes both the trityl and the fluoride ion in their free form, leading to mildly acidic values. **4a** has an FIA_{DCM} of only 36, **4c** of 47, and **4d** of 74 kJ mol^{-1} while Ph_3C^+ reaches 175 kJ mol^{-1}. The HIA_{gas} values are only 100–150 kJ mol^{-1} lower than those of the unsubstituted trityl cation. They range from 684 (**4a**) to 720 (**4c**) kJ mol^{-1} in the gas phase and 185 (**4a**) to 209 (**4c**) kJ mol^{-}1 in DCM. The utilized donor substituents stabilize the carbocations and thus, lower their acidity. Particularly the *HIA*s remain considerable, suggesting promise as stable organic Lewis acids (**Table 2**).

Table 2. Fluoride and hydride ion affinities of the cationic units of the salts **4** and triphenylmethylium in the gas phase and in dichloromethane (DCM).

	 4a	 4c	 4d	 ph_3C^+
FIA_{gas} (kJ mol^{-1})	451	476	504	648 (cf. 599[19a])
FIA_{DCM} (kJ mol^{-1})	36	47	74	175
HIA_{gas} (kJ mol^{-1})	684	707	722	829 (cf. 801[19a])
HIA_{DCM} (kJ mol^{-1})	185	195	209	277

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3. Conclusion

We have discovered a straightforward synthesis of methoxylated trityl cations with a Friedel–Crafts acylation–alkylation cascade utilizing arenes and acylium ions created in situ from carboxylic acids with triflic anhydride. This was successfully shown for three distinct trityl cations including unsymmetric products. This approach is notable for bypassing the need for multistep processes and external C1 sources. While the method needs further improvements, our findings may pave the way for more sustainable and efficient routes to electron-rich trityl ions.

4. Experimental Section

Experimental Methods

All synthetic procedures were carried out in a glovebox (O_2 and $H_2O < 5$ parts per million) or in Schlenk glassware in a dry argon atmosphere unless stated otherwise. NMR experiments were prepared in a glovebox and performed in tubes closed with rubber septa. Glassware used in these procedures was preheated in an oven at 120 °C for at least 2 h and flame-dried with a heat gun and flushed with dry argon thrice.

Computational Methods

Conformers were selected with a pipeline using autodE 1.4.3,[30] ETKDGv3 in RDKit v. 2024.3.3,[31] and GFN2-xTB[32] with optional generalized Born solvation model with hydrophobic solvent-accessible surface area for DCM[33] in xTB 6.5.1.[34] at the GFN2-xTB level.[32] A stable selection of structures was preoptimized with loose restraints in ORCA 5.0.4[35] at the r^{2}SCAN-3c[26a]/RIJCOSX[26b] with optional conductor-like polarizable continuum model solvation for DCM.[29] The best conformer of a molecule was fully optimized and its Hessian was computed with the same method. autodE was used to compute the zero-point energy and free energy corrections based on Hessians generated at the same level of theory. Potential imaginary frequencies smaller than 40 cm^{-1} were not considered transition states and were treated as real frequencies within thermochemistry calculations (multiplication by $-i$). Low-frequency vibration modes were treated with the quasirigid-rotor-harmonic-oscillator approximation with $\omega_0 = 100\ cm^{-1}$.[36] Energies were calculated at a 1 M concentration and a temperature of 25 °C.

Reaction of Bis(2,4,6-Trimethoxyphenyl)methanone 3a with Tf_2O

Bis(2,4,6-trimethoxyphenyl)methanone **3a** (10.9 mg, 30.1 μmol, 1.00 eq.) was put in an NMR tube under argon with 650 μL of $CDCl_3$. Tf_2O (9.6 mg, 34 μmol, 1.13 eqs.) was added; then the NMR tube was heated to 50 °C for 125 h 55 min. This reaction formed tris(2,4,6-trimethoxyphenyl)methylium triflate **4a** in 18% yield.

Reaction of Bis(2,4,6-Trimethoxyphenyl)methanone 3a and 1,3,5-Trimethoxybenzene 2a with Tf_2O

Bis(2,4,6-trimethoxyphenyl)methanone **3a** (10.9 mg, 30.1 μmol, 1.00 eq.) and 1,3,5-trimethoxybenzene **2a** (6.0 mg, 35 μmol, 1.10 eq.) were put in an NMR tube under argon with 700 μL of $CDCl_3$. Tf_2O (9.7 mg, 34 μmol, 1.13 eqs.) was added; then the NMR tube was heated to 50 °C for 125 h 55 min. This reaction formed tris(2,4,6-trimethoxyphenyl)methylium triflate **4a** in 32% yield.

Reaction of 1,3,5-Trimethoxybenzene 2a with Tf_2O

1,3,5-Trimethoxybenzene **2a** (5.0 mg, 30 μmol, 1 eq.) was put in an NMR tube with 650 μL of dry $CDCl_3$. Tf_2O was added, then the NMR tube was heated to 50 °C for 64 h. No reaction was observed.

*Decomposition of 2,4,6-Trimethoxybenzoic acid **1a** in $CDCl_3$*

2,4,6-Trimethoxybenzoic acid **1a** (10.0 mg, 47.1 μmol) was solved under air 1) in 650 μL of $CDCl_3$, 2) in 650 μL of $CDCl_3$ that was stored over 4 Å molecular sieves, and 3) in 650 μL C_6D_6. Then, NMR spectra of the samples were measured regularly at room temperature. 1) The relative integrals after 2 h indicated that the mixture consisted of 97% **1a** and 3% **2a**. After 97 h, the relative integrals indicated that the mixture consisted of 40% **1a** and 60% **2a**, indicating in situ formation of **2a**. 2) and 3) No new signals were observed.

Reaction of Bis(2,4,6-Triisopropylphenyl)methanone 3b with Tf_2O

Bis(2,4,6-triisopropylphenyl)methanone **3b** (13.5 mg, 31.1 μmol, 1.00 eq.) was put in an NMR tube under argon with 650 μL of $CDCl_3$. Tf_2O (8.8 mg, 31 μmol, 1.00 eq.) was added; then the NMR tube was heated to 50 °C for 62 h, after which it was heated to 60 °C for 252 h for a total of 313 h of heating time. The formation of 1,3,5-triisopropylbenzene **2b** was observed and confirmed by GCMS.[37]

Reaction of Bis(2,4,6-Triisopropylphenyl)methanone 3b with TfOH

Bis(2,4,6-triisopropylphenyl)methanone **3b** (13.0 mg, 29.9 μmol, 1.00 eq.) was put in an NMR tube under argon with 650 μL of dry $CDCl_3$. TfOH (32.8 mg, 214 μmol) was added in excess, resulting in an immediate color change from colorless to a yellow/red color. The sample was left at room temperature for 168 h. Unspecific decomposition was found.

Reaction of 2,4,6-Triisopropylbenzoic Acid 1b with Tf_2O

2,4,6-Triisopropylbenzoic acid **1b** (8.0 mg, 31 μmol, 1.00 eq.) was put in an NMR tube under argon with 650 μL of dry $CDCl_3$. Tf_2O (10.0 mg, 34.7 μmol, 1.00 eq.) was added; then the NMR tube was heated to 50 °C for 90 h 31 min. The formation of 1,3,5-triisopropylbenzene **2b** was observed.[37]

General Procedure for Trityl Cation Syntheses in NMR Scope

Carboxylic acid (30.0 μmol) and arene (60.0 μmol, 2.00 eqs.) were put in an NMR tube under argon with 650 μL of $CDCl_3$. Tf_2O (30.0 μmol) was added. The NMR tube was heated to 50 °C for 132 h. Yields were determined via qNMR with hexamethylbenzene as internal standard.

General Procedure: Preparation of Trityl Salts

Carboxylic acid (1.00 eq.) and arene (2.00 eq.) were put in a Schlenk flask under argon with 10 mL/mmol dry $CHCl_3$. Tf_2O (1.25 eqs.) was added. The mixture was heated to 50 °C under stirring for 72 h. The crude was dried in vacuo and the product was isolated via flash chromatography (*n*-pentane/ethyl acetate 3:1, then ethyl acetate, then ethyl acetate/methanol 3:1).

Tris(2,4,6-Trimethoxyphenyl)methylium Triflate 4a

This compound was synthesized following the general procedure from 2,4,6-trimethoxybenzoic acid **1a** (2.20 g, 10.2 mmol, 1.00 eq.),

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1,3,5-trimethoxybenzene **2a** (3.43 g, 20.2 mmol, 1.98 eqs.), triflic anhydride (3.56 g, 12.5 mmol, 1.23 eqs.), and 100 mL of dry $CHCl_3$. The product was received as a deep blue solid (3.12 g, 4.71 mmol, 46%). NMR spectral data were in accordance with available data for the chloride and tetrafluoroborate of the same cation.[15] ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.02 (s, 6H, **4**), 3.95 (s, 9H, **7**), 3.56 (s, 18H, **6**). ^{13}C NMR (151 MHz, $CDCl_3$): δ 169.8 (3C, **5**), 166.8 (1C, **1**), 164.1 (6C, **3**), 118.7 (3C, **2**), 91.6 (6C, **4**), 56.6 (6C, **6**), 56.4 (3C, **7**). ^{19}F NMR (565 MHz, $CDCl_3$): δ −78.5 (TfO^-). HRMS: m/z calc. for $[C_{28}H_{33}O_9]^+$: 513.21191. Found: 513.21362. ATR-IR (neat) 3100 (vw), 3001 (w), 2945 (w), 2843 (w), 2619 (w), 2380 (vw), 2106 (vw), 1585 (vs), 1553 (s), 1451 (s), 1415 (s), 1365 (vw), 1221 (vs), 1152 (vs), 1113 (vs), 1060 (s), 1021 (vs), 945 (s), 924 (s), 888 (s), 816 (s), 745 (m), 681 (m). Crystallographic analysis is described in the supporting information.

2,4,6-Trimethylphenylbis(2,4,6-Trimethoxyphenyl)methylium Triflate 4c

This compound was synthesized following the general procedure from 2,4,6-trimethylbenzoic acid **1c** (169 mg, 1.03 mmol, 1.00 eq.), 1,3,5-trimethoxybenzene **2a** (343 mg, 2.02 mmol, 1.96 eqs.), triflic anhydride (356 mg, 1.25 mmol, 1.21 eqs.), and 10 mL of dry $CHCl_3$. The product was received as a deep purple oil (85 mg, 139 μmol, 14%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.73 (s, 2H, **10**), 6.06 (s, 4H, **4**), 4.03 (s, 6H, **7**), 3.55 (s, 12H, **6**), 2.25 (s, 3H, **13**), 1.86 (s, 6H, **12**). ^{13}C NMR (151 MHz, $CDCl_3$): δ 177.5 (**5**, 2C), 173.6 (**3**, 4C), 165.7 (**1**, 1C), 141.1 (**9**, 2C), 139.4 (**11**, 1C), 136.7 (**8**, 1C), 128.6 (**10**, 2C), 121.0 (**2**, 2C), 120.3 (q, TfO^-, 1C), 92.1 (**4**, 4C), 57.1 (**7**, 2C), 56.8 (**6**, 4C), 21.2 (**13**, 1C), 20.3 (**12**, 2C). ^{19}F NMR (564 MHz, $CDCl_3$): δ −78.5 (TfO^-). HRMS: m/z calc. for $[C_{28}H_{33}O_6]^+$: 465.22717. Found: 465.22671. ATR-IR (neat, taken after additional purification, see Supporting Information) 3472 (w), 3203 (vw), 3140 (w), 2924 (vs), 2851 (s), 2658 (w), 2445 (vw), 2363 (vw), 2292 (vw), 2225 (vw), 2185 (vw), 2106 (vw), 1941 (vw), 1897 (vw), 1810 (vw), 1597 (vs), 1550 (vs), 1478 (vs), 1445 (vs), 1420 (vs), 1375 (vs), 1233 (vs), 1160 (vs), 1124 (vs), 1060 (s), 1026 (vs), 925 (s), 894 (s), 829 (s), 785 (w), 738 (s), 695 (m), 636 (vs), 585 (s), 517 (s), 495 (m), 485 (vw).

Phenylbis(2,4,6-Trimethoxyphenyl)methylium Triflate 4d

This compound was synthesized following the above procedure from benzoic acid **1d** (123 mg, 1.00 mmol, 1.00 eq), 1,3,5-trimethoxybenzene **2a** (346 mg, 2.03 mmol, 2.03 eqs.), triflic anhydride (356 mg, 1.25 mmol, 1.25 eqs.), and 10 mL of dry $CHCl_3$. The product was received as a deep green solid (487 mg, 850 μmol, 85%). Due to presumably low-boiling impurities seen in the ^{1}H NMR spectrum, the material was heated to 100 °C in vacuo over night before filtration in dichloromethane over Celite. This gave the product as deep green solid (123 mg, 215 μmol, 21%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (t, J = 7.4 Hz, 1H, **11**), 7.38 (t, J = 7.9 Hz, 2H, **10**), 7.30–7.25 (m, 2H, **9**), 6.15 (s, 4H, **4**), 4.08 (s, 6H, **7**), 3.55 (s, 12H, **6**). ^{13}C NMR (151 MHz, $CDCl_3$): δ 177.8 (1C, **1**), 173.5 (2C, **5**), 165.7 (4C, **3**), 144.8 (1C, **8**), 133.1 (1C, **11**), 131.9 (2C, **9**), 128.3 (2C, **10**), 119.4 (2C, **2**), 92.4 (4C, **4**), 57.2 (2C, **7**), 56.6 (4C, **6**). ^{19}F NMR (565 MHz, $CDCl_3$): δ −78.4 (TfO^-). HRMS (taken before final drying and filtration): m/z calc. for $[C_{25}H_{27}O_6]^+$: 423.18022. Found: 423.17997. ATR-IR (neat) 3105 (vw), 2936 (vw), 2851 (vw), 2735 (vw), 2435 (vw), 2395 (vw), 2293 (vw), 2195 (vw), 2165 (vw), 2065 (vw), 2033 (vw), 1988 (vw), 1947 (vw), 1905 (vw), 1880 (vw), 1738 (vw), 1592 (vs), 1546 (m), 1476 (s), 1447 (s), 1420 (m), 1373 (w), 1232 (vs), 1150 (s), 1122 (vs), 1024 (s), 942 (w), 913 (w), 827 (m), 793 (w), 760 (m), 698 (m), 661 (vw).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in [ioChem-BD] at [https://pubs.acs.org/doi/full/10.1021/ci500593j].

Keywords: acids · carbocations · Friedel–Crafts acylations · Lewis acids · trityl cations

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